

VERY HIGH FREQUENCY EPR SPECTRA OF ORGANIC SULFUR COMPOUNDS

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ABSTRACT

Radical cations formed from several sulfur-containing heterocyclic aromatic compounds have been studied, both as subjects in their own right and as models for organic sulfur in coal. Since for most organic radicals, the g shift and g anisotropy are expected to be small, they have seldom been resolved at conventional X-band (9.5 GHz) EPR. Our very high frequency (VHF) EPR spectrometer (W-band, 95 GHz) provides a tenfold increase in spectral resolution, which enables us to obtain, for the first time, the principal g matrices of thiophenic radical cations in amorphous or disordered state. The EPR experimental results are presented, along with observation of certain trends of g shift and g anisotropy among the homologous series.

INTRODUCTION

Identification of the chemical forms of sulfur-containing heterocyclic aromatic compounds in coal continues to be a challenging problem. Our previous studies¹ hypothesized that the very high frequency (VHF) EPR spectra of Illinois #6 coal could be approximated by superposition of two main classes of organic radicals. The first class was polycyclic aromatic hydrocarbon radicals and the second was the radicals from heterocyclic aromatic compounds containing sulfur, oxygen, or nitrogen. It was suggested that the spin-orbit coupling from sulfur could be responsible for the low field feature of the W-band spectra of the coal.

In order to fully explore this hypothesis, we are investigating a number of sulfur- and oxygen-containing organic radical ions by VHF EPR spectroscopy. The goal is to obtain their anisotropic g -factors and to assess the influence of heavy atoms such as sulfur and oxygen and extent of aromatic conjugation on EPR parameters, especially g anisotropy and EPR line-shape. Here we present some of our experimental results on cation radicals from thiophenic compounds.

The g -factor, one of the most important and fundamental EPR parameters, characterizes the position of a resonance signal: $g = h\nu/\beta B_0$, where B_0 is external magnetic field strength at the resonance (also called spectral center or resonance field center). A g -factor for a molecule containing an unpaired electron is generally viewed as characteristic of its electronic structure. But there are several reasons which can prevent the g -factor from being a straightforward and definitive structural indicator.

For most organic radicals, g -factors are very close to the free-electron value ($g_0 = 2.00232$). The g shift, $\Delta g = g - g_0$, is consequently small. A typical Δg for carbon centered radicals is ca. 20×10^{-5} and only several-fold greater for heterocyclic containing oxygen or sulfur. Experimentally resolving such small g shifts is difficult, especially in non-single-crystal solids (powders, frozen solutions, glasses) where the situation is more complicated.

Since for most cases, g -factors are intrinsically anisotropic, due to spin-orbit coupling, the resonance field positions vary with the orientation of the molecules in the external magnetic field. Therefore, g is represented as a matrix with three principal values. If molecules are tumbling rapidly, then the g matrix is motionally averaged to a single average (scalar) value $\langle g \rangle = (g_1 + g_2 + g_3)/3$, where $\langle g \rangle$ determines the averaged resonance line center. In a disordered solid, the resonance spectrum will be a superposition of the individual absorption spectra of the variously-oriented molecules. In the typical macroscopically isotropic specimen, the whole ensemble assumes with equal probability every possible orientation relative to the external magnetic field. The resulting composite is known as a powder spectrum. Principal g matrix values or components can still be resolved providing that extreme g values differ enough. But as stated earlier, for most organic radicals the g values are all quite close together. Thus, under the effect of other line broadening mechanisms, powder spectra of organic radicals often show a single, featureless (and boring) line with varied width and symmetry and very limited information content, as illustrated in Fig. 1(a).

One possible way to overcome this problem is to work at higher magnetic fields (requiring higher microwave frequency) to enhance the spectral resolution.² From the simple resonance condition one can see easily that the difference in resonance fields corresponding to slightly different g -factors is proportional to the product of the microwave frequency with the difference in g -factors. Therefore the spectral resolution will be enhanced by a factor of 10 in going from X-band (9.5 GHz) to W-band (95 GHz) providing the line does not broaden substantially with microwave frequency. Fig. 1(b) demonstrates this greatly enhanced g -resolution.

Thiophenic compounds have been thought to be abundant in Illinois coal³. Upon chemical oxidation on catalyst surface or UV irradiation in boric acid glass, such compounds yield immobilized and extremely long-lived cation radicals suitable for EPR studies. EPR spectra of the radical cations so prepared from thiophene and four more structurally related compounds were obtained at both X-band and W-band frequencies. The principal g matrix components obtained from analyses of these spectra are reported here. We have found in the literature no previous reports of g matrices for these radicals.

EXPERIMENTAL SECTION

Thiophene (THI), benzothiophene (BTH), dibenzothiophene (DBT) and benzo[*b*]naphtho-[2,1-*d*]thiophene (BNT) were purchased from Aldrich; dinaphthylene thiophene (DNT), from ICN. The highest commercially available grades (typically 99+% pure) were obtained and used without further purification.

To generate free radical ions, we have tried several different methods. Two of them proved to be quite versatile and thus are used routinely. The first is chemical oxidation at a metal oxide

catalyst surface with O_2 ; the catalysts can be either alumina or alumina/silica like Houdry M46. The second is UV photolysis in boric acid glass. Both methods can produce sufficient populations of stable radical ions in a powder or glassy matrix, thus mimicking the disordered state of chemical species in coal.

In method I, γ -alumina from Akzo was loaded into an EPR tube attached to a three-way Y-shaped connector with a connector to vacuum line and a septum seal. After the alumina was calcined at ca. 650 °C for 12 hours, a small amount of gaseous oxygen was let in for about 4 hours. The benzene solution of the thiophenic compound was injected onto the alumina to form a suspension. Over some time (a few minutes to several days), the color developed which indicates formation of radical ions. The suspension was then freeze-thaw-pumped (three cycles) to deplete the oxygen. The EPR tube was then flame-sealed. A W-band sample prepared this way can be used in both X-band and W-band resonators.

In method II, a mixture of powdered boric acid and the desired thiophenic compound (1000:1 mole ratio) is heated to the melting point of boric acid (ca. 180 °C). The molten mass is allowed to cool to a glass, broken into small fragments or crashed into fine powder, and loaded into a quartz sample tube. The tube is placed in a Ray-O-Net irradiation unit and subjected to UV irradiation at 254 nm for 30 minutes. The sample tube is then removed and sealed for analysis. Samples of cation radicals still give the same strong EPR signal even one year after their preparations.

X-band spectra were obtained from a Varian E-line 12" EPR spectrometer outfitted with a tracking Varian NMR gaussmeter and a Fluke frequency counter. Different microwave levels were used to ensure no power saturation, and different magnetic field modulation amplitudes were used to find the best balance between S/N and resolution. W-band EPR was performed on a locally-built spectrometer described elsewhere (reference 1). All radicals have been prepared at least three times and each sample run at least four times.

The resolution of W-band spectra is usually so high that one can read the principal g matrix directly, which is impossible at much lower frequencies. Nevertheless, a computer-assisted analysis using an EPR powder spectrum simulation program² was still performed to confirm the direct measurements.

RESULTS AND DISCUSSION

The g-shifts at W-band and X-band and the measured principal g-matrix components of the heterocyclic sulfur cation radicals are summarized in Figs. 2 and 3.

The g shifts measured at X-band seems compare well with those measured at W-band. Actually, g shift measurement at W-band have more than three times better accuracy than at X-band, because not only is the W-band g shift calculated as an average of three separately measured individual matrix components, each better defined spectroscopically than the line center measured at X-band. It is rather difficult to define the resonance center for a usually broad and asymmetric line.

There is a general agreement between g shifts measured for the alumina surfaces and those for the corresponding boric acid glasses (Fig. 2). But this agreement should not be viewed as proving that these two different preparations yield precisely the same radical species; comparison of the full g -matrices would be much more revealing. Moreover, careful analysis of the g matrices might result in additional information on these radical ions.

It is also observed that g shift or g matrix components do not follow a monotonic trend among our series (Fig. 2). Rather, the g shift starts from THI, rises up, peaked at DBT, then falls down toward DNT. Also, the lowest field g matrix component g_1 and g_2 behave similarly while g_z stays constantly near the free-electron g value (Fig. 3). The latter is expected because all these radicals are planar π radicals, where delocalized p_z electrons have zero shift on g_z .

The fact that both g shift and two of the three principal g -matrix values vary substantially with the number of fused benzene rings is very encouraging. It demonstrates that W-band EPR spectroscopy of these organic sulfur radicals is very sensitive to their structures. Thus the EPR parameters of those model compounds, especially anisotropic g values, have the potential to help identify the sulfur-containing heterocyclic moieties in coal. Clearly, studies on more model compounds are needed in order to build a library of VHF EPR spectra. We are currently investigating a dozen more alkyl-thiophenes or benzothiophenes as well as an analogous furanic series.

Based on notions including 'frozen orbitals' and additive property of g shifts, Stone⁴ proposed the g shift of aromatic hydrocarbon to be $\Delta g = b + \lambda C$ where λ is the coefficient in the simple Hückel Molecular Orbital (HMO) energy expression $E = \alpha + \lambda\beta$, where α and β are the Coulomb and resonance integral, respectively; b and c are empirical parameters. Fig. 4 shows the measured g shift plotted against λ from HMO's. It seems that four of the five points fall into a straight line in this particular sulfur heterocyclic series. We are a bit surprised by this observation in view of the crudity of this simple treatment. We cannot guarantee that this 'correlation' is not accidental; more experimental examples are required to establish a generalization at a high level of confidence.

Fig. 5, 6, and 7 show g matrix components (g_1 , g_2 and g_3), g shift, and g_{xy} anisotropy vs. spin density calculated by McLachlan's method of perturbation on HMO⁵. Fig. 5 indicates that both g_1 and g_2 increase with the π spin density, with g_1 faster than g_2 . Fig. 6 shows that the g shift also increases with the π spin density at the sulfur atom. From Fig. 7 one sees that the difference between g_1 and g_2 (so called xy anisotropy) increases with the π spin density at the sulfur atom. These probably suggest that one of the g matrix components g_1 is more sensitive to the change of π spin density distribution in the aromatic ring. One tentative conclusion from these comparisons of theory and experimental data is that one of the g matrix components, g_1 , is more sensitive to the change of π spin density distribution in the aromatic ring than the others. We are currently using more elaborate MO calculations to examine how structural features other than the number of benzene rings should affect the anisotropic g values.⁶

SUMMARY

Radical cations prepared from thiophene and some of its aromatic homologues were studied by

a novel technique — VHF (W-band) EPR spectroscopy. The first unambiguous results on principal g matrices and g shifts for these species are presented. Since the EPR parameters determined from W-band spectra of these compounds prove very sensitive to their molecular structure, this technique is promising for the nondestructive analysis of the chemical forms of organic sulfur in coal, where nearly identical g -factors have been observed and correlated with organic sulfur content¹.

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Fig. 1. EPR spectra of dibenzothiophene (DBT) cation radical in boric acid glass. a) At X-band, b) At W-band.

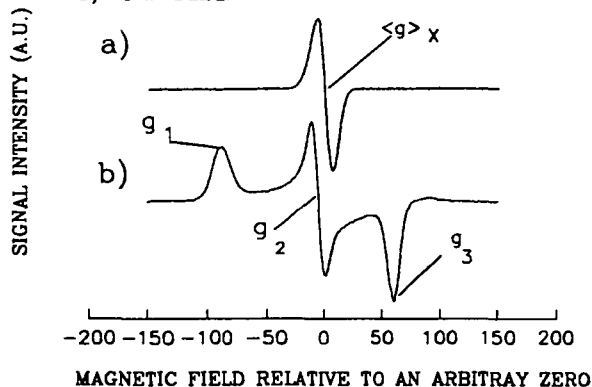


Fig. 2. g-shifts of thiophenic cation radicals on alumina (A) surface and in boric (B) acid glass.

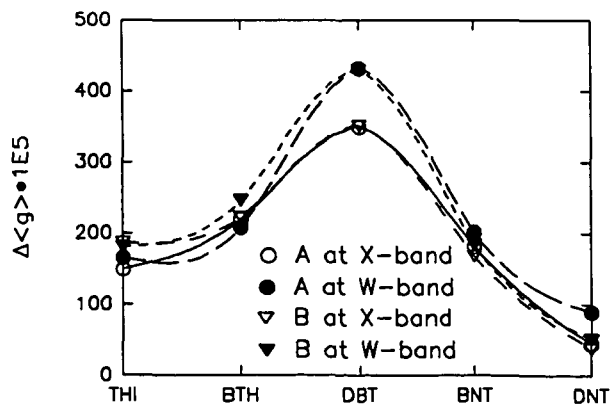


Fig. 3. Measured three principal g -matrix components, (A) on alumina (B) in boric acid glass

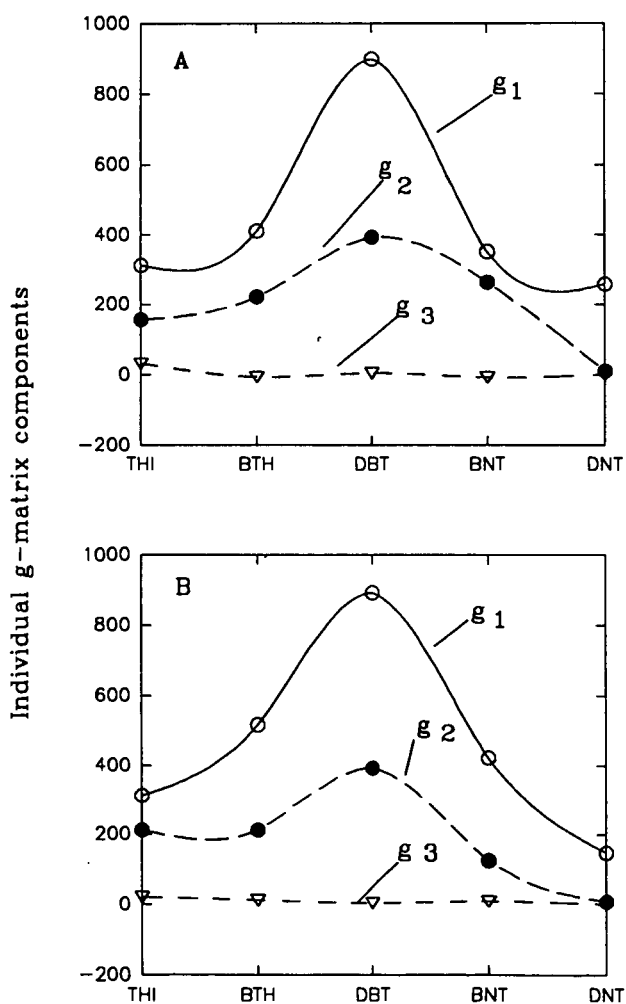
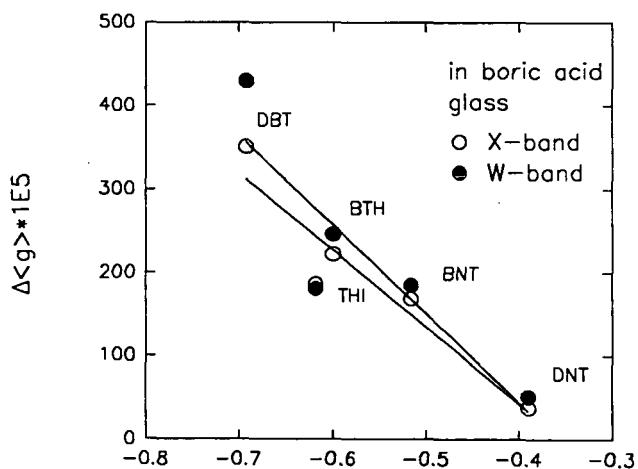
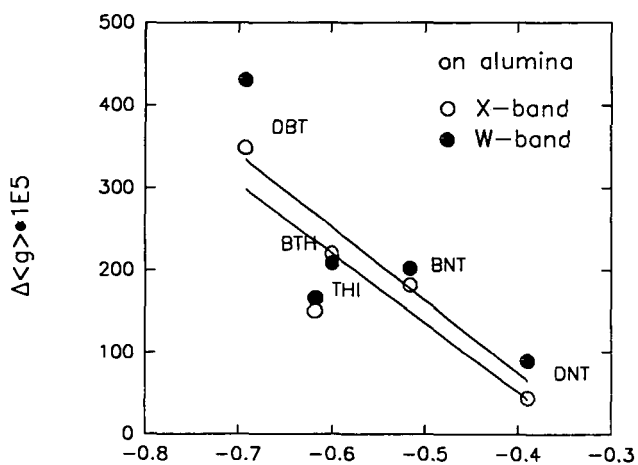


Fig. 4. Experimental g-shifts plotted against λ in HMO calculation.



λ in HMO

Fig. 5. A plot of principal g-matrix components against calculated π spin density on sulfur

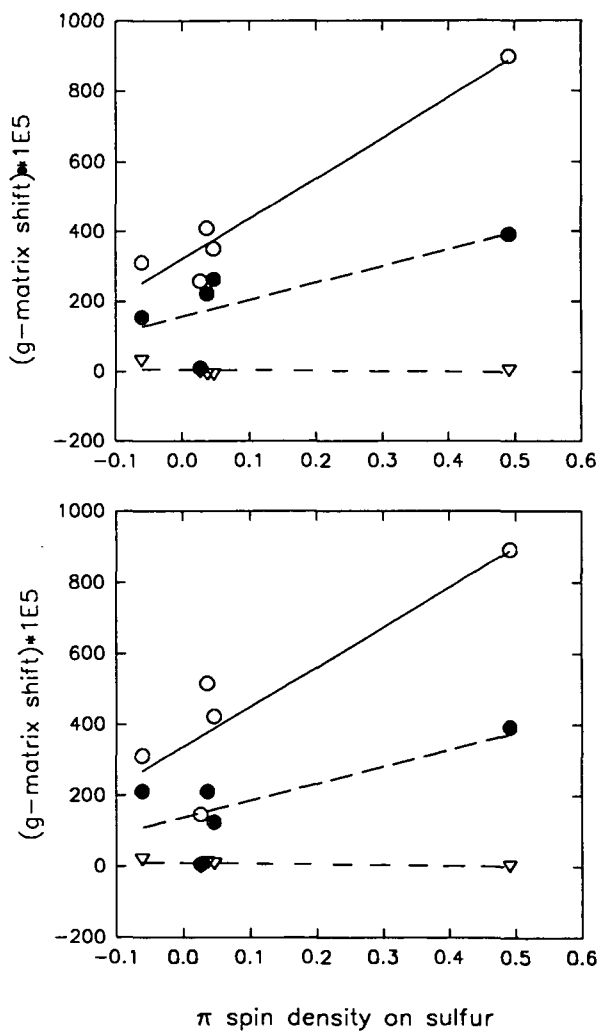


Fig. 6. A plot of g-shift at W-band vs. calculated π spin density on sulfur

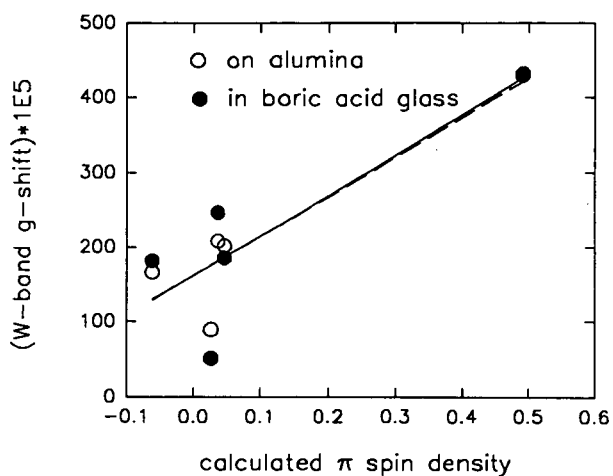


Fig. 7. g xy anisotropy vs. calculated π spin density on sulfur

